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SULPHUR OXIDES
SULPHUR-35
TRACER TECHNIQUES

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PHYSICAL AND CHEMICAL PROCESSES OF SULPHUR DIOXIDE IN THE PLUME FROM AN OIL-FIRED POWER STATION

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ABSTRACT

The Danish contribution to the EUROCOP COST 61a project is described. Work concerned the physical and chemical reactions of sulphur dioxide released from a power station.

The investigation was based on the application of two tracers. Inactive, inert SF_6 is used to monitor the dispersion of and deposition from the plume; it was intended to use radioactive $^{35}SO_2$ to determine the degree of oxidation of sulphur released from the stack; so far, however, public reaction has prevented the use of a release of activity in field experiments.

The report describes the construction and testing of airborne instruments for continuous registration of sulphur dioxide, nitrogen oxides, ozone and the tracer SF_6, as well as for measurements of temperature and humidity. Sulphur samples were collected on filter paper in a specially constructed low volume air sampler, and the subsequent chemical analysis in the laboratory is described. Finally, the problem of navigation is treated.

It is shown that nitrogen oxides may be used as an internal tracer in plume experiments. Preliminary experiments based on inactive analysis only indicated an overall half-life for SO_2 in the plume of about half an hour.

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PREFACE

In the agreement signed in Brussels on November 23, 1971, by:

> the Governments of
> Denmark, The Federal Republic of Germany, Spain, The French Republic, Greece, The Italian Republic, The Kingdom of the Netherlands, The Socialist Federal Republic of Yugoslavia, The Republic of Austria, The United Kingdom of Great Britain and Northern Ireland, and
> The European Coal and Steel Community

the following definition is given of COST - Project 61a "Research into the Physico-Chemical Behaviour of SO_2 in the Atmosphere":

> "The project is concerned with the clarification of the physico-chemical behaviour of sulphur dioxide in the atmosphere. The term "physico-chemical behaviour" is taken to mean all the reactions occurring in the atmosphere which lead to a change in the state of sulphur dioxide or in the course of which sulphur dioxide undergoes a chemical transformation which decisively influences its further behaviour or the behaviour of its reaction products".

The Danish contribution to the project was an investigation of the dispersion and the physical and chemical reactions of sulphur dioxide released from a power station. Studies started in 1972 and the various experimental preparations and test experiments were described in a series of progress reports.

Unlike the former reports, the present one is published in the open literature; it was therefore prepared as a self-contained publication and consequently contains some previously reported material. This applies especially to the descriptions of instruments and analytical techniques.

By the end of the project period, November 1976, only preliminary results have been obtained, but it is planned to continue the measurements.

1. INTRODUCTION

Sulphur dioxide formed by the combustion of fossil fuels is one of the major air pollutants. It is debatable whether it is harmful in the observed concentrations, but harmful effects certainly appear when SO_2 is oxidized to SO_3 and then forms sulphuric acid or sulphates. H_2SO_4 may cause considerable corrosion of construction materials and may increase the acidity of rain, watercourses and lakes, thus harming animal and plant life. The effects on human health are related to the tendency of H_2SO_4 to attach itself to aerosol particles that can penetrate to the lungs. Studies of the conversion of SO_2 in the atmosphere are therefore just as important as studies of its distribution.

In 1969 Urone and Schroeder published a paper called: "SO_2 in the atmosphere: A wealth of monitoring data, but few reaction rate studies" with the subtitle: "Study of the reactions of SO_2 - a vital due to the chemistry of polluted atmospheres - is beset with difficulties". Now - years later - the situation is not much changed.

1.1. Previous investigations of sulphur dioxide conversion

Several laboratory studies of simple systems (e.g. Smith and Urone 1974) have concerned the oxidation of sulphur dioxide and shown the influence of light and humidity, the reactions with other components (e.g. NO_2), and the importance of catalysts such as manganese. The results, however, are difficult to apply to the much more complex situation in the free atmosphere, and only recently has any attempt been made (Freiberg 1976) to formulate a comprehensive model of the reactions in a dispersing plume. On the other hand, it is difficult to harmonize the results of studies in the free atmosphere - and sometimes even difficult to compare them because the types of reaction are unknown.

Some of the earliest field studies were performed by Meetham (1950, 1954) who estimated that the average lifetime of a SO_2 molecule in Britain was less than 12 hours. In the London fog

of 1952 it was only 6 hours. Even lower values were found (Weber 1970) from ground-based investigations in Frankfurt-am-Main. CO_2 was used as a tracer; both CO_2 and SO_2 emissions are well known: CO_2 is practically inert, whereas the proportion of SO_2 can decrease by oxidation or absorption during transport in the atmosphere. Weber found that about 50% of the emitted SO_2 was lost in 20 minutes to 1 hour depending upon the meteorological conditions.

Conversion during long-range transport has been investigated, for example, by Eliassen and Saltbones (1975), who collected daily mean concentrations of SO_2 from several OECD ground sampling sites in Europe. The results were compared with a trajectory model that included the rates of decay, transformation and absorption of SO_2; best agreement was obtained by assuming a residence time for SO_2 of about half a day. The transformation to sulphate corresponds to a rate an order of magnitude lower.

In another long-range study Prahm et al. (1976) measured SO_2 and trace metal concentrations on the Faroes and on the British Isles. Since there are practically no sources between these two localities, concentration differences for air masses which had moved between the two localities along calculated trajectories could be used to determine an eddy deposition rate for SO_2 and sulphate corresponding to deposition velocities of 2 cm/s and 0.5 cm/s respectively. The transformation rate for SO_2 to sulphate was estimated to correspond to a half-life of about 50 hours.

Measurements directly in a plume were probably first performed by Gartrell, Thomas and Carpenter (1963), who collected SO_2 and sulphate samples from a helicopter at various cross sections in the plume from a coal-fired power plant. They found oxidation rates of up to 2% per minute, depending upon the position in the plume and the relative humidity.

In a more recent study Stephens and McCalding (1971) measured SO_2 and particulate matter, using an aircraft for distances up to 80 km from a coal-fired power station. Particles were used as a conservative tracer to follow the SO_2 decay. Half-lives of 70 min, 144 min and ∞ were found with decreasing

humidity (80-30%). No distinction was made between absorption and oxidation.

Davies, Smith and Klauber (1974) used an aircraft for following the plume from a power station using a mixture of oil and coal. The main objective was to study ozone production and most of their measurements apply to NO → NO_2 conversion, but they suggest that an oxidation of SO_2 may correspond to a half-life of about 10 hours.

All these experiments have the inherent drawback that an estimation of the loss of SO_2 through oxidation and of that through deposition is difficult - if not impossible. This distinction requires the use of at least two tracers: one, inert, to monitor the dispersion of the plume and one that follows the sulphur. In a very extensive work, Manowitz and co-workers from BNL (Newman, Forrest and Manowitz 1975) used SF_6 as inert tracer and the ratio between ^{32}S and ^{34}S in the sample as a tracer for sulphur in conjunction with simultaneous concentration measurements of sulphur dioxide and sulphate. Assuming a pseudo second-order reaction mechanism depending upon sulphur dioxide and particulate concentrations, they determined a rate constant of 1 $ppm^{-1}h^{-1}$ in the plume from an oil-fired power station. The reactions seemed to be slower for a coal-fired plant. The rates did not appear to depend upon the humidity.

The majority of the investigations within the COST 61a project were performed in the laboratory, but a few experiments and notably one performed by Cox and Eggleton at Harwell had a more "realistic" approach. Ambient air was collected in plastic bags "spiked" with radioactive SO_2 and exposed to sunlight. The rates of SO_2 oxidation varied between 0.1 and 2.3% per hour and showed a significant correlation both with the production of ozone during exposure and with the concentration of hydrocarbons and nitrogen oxides present initially in the air samples. On the basis of the results, empirical expressions were derived for the prediction of atmospheric SO_2 oxidation rates in polluted air. Maximum summer daytime oxidation rates for conditions in London were calculated to be up to 7% per hour - winter values probably being 3-5 times lower. This corresponds to half-lives of about

10 and 40 h, respectively.

Some of the COST experiments aimed at measurements in the free atmosphere, but only two determined SO_2 processes directly. One was a German project carried out by Baltrusch and Bingemer. By means of airborne measurements using CO_2 as a tracer, investigations were made of the dispersion and conversion of SO_2 from the entire Ruhr industrial area. Thus the results represented average values from a series of "events" with different emitters in different surroundings. So far, a modest conversion is indicated over distances of the order of hundreds of km.

The other field investigation of SO_2-processes, performed under the COST 61a project, was carried out in Denmark and is the subject of the present report.

All the different COST projects will be reviewed in a forthcoming report.

1.2. Plan of the Danish COST 61a experiment

With the aim of clarifying the fate of sulphur dioxide, it was decided to study the effluent from a single power station at distances up to 100 km with respect to the following:

1) The variation of the concentration of sulphur dioxide and sulphate inside the plume,

2) Concentrations of ozone and nitrogen oxides inside and outside the plume,

3) Composition and size distribution of particulate matter in the plume, and, finally,

4) The humidity and temperature of the plume.

It is necessary to use two tracers; one, chemically inactive and stable, was used to trace the plume and to measure the degree of dispersion and sedimentation; sulphur hexafluoride was chosen for this purpose (cf. sect. 2.1). The other tracer was a radioactive isotope of sulphur (^{35}S), which was to be emitted from

the stack in the form of SO_2; it would serve to determine the degree of chemical conversion (cf. sect. 2.2).

It would have been quite impossible to mount the necessary instruments in the form of ground-level, fixed or mobile sampling stations, for this would have required a multiplicity of sampling equipment and personnel and a degree of mobility unachievable in practice. It was therefore decided to mount the required instruments in an aircraft (cf. chapter 3) in which cross-plume and upwind traverses would be made.

As the measurements took place at distances where the plume is not visible, the localizing constituted a major problem. Further, it was obvious that, for interpretation of the data, it would be necessary to correlate the data measured in the air to a coordinate system on the ground with a reasonable spatial uncertainty, as compared to the dimensions of the plume. This was accomplished by special use of Decca navigation instruments (sect. 5.2).

In view of the fact that a comparatively well defined and stable plume is required for measurements of this nature, weather conditions such as atmospheric stability, wind vector distribution, inversions, etc., must be known. This made meteorology an important part of the experiments (sect. 5.1).

So far, public reaction has prevented the release of radioactivity into the atmosphere. Thus the results of field measurements presented in this report are all obtained by inactive analysis.

1.3. The Stigsnæs power plant

The experiments were carried out at the Stigsnæs power plant situated on the south-west coast of Zealand. In its immediate vicinity are a Gulf oil refinery and a small town (Skælskør) without heavy industry; otherwise the surroundings are rural (Fig. 1). The plant has two separate units each with a 130 m high stack. Both units are fired with oil that contains on the average about 2.5% sulphur; at full power (435 MW brutto) the total SO_2 emission is about 4.45 t/h. The emission from the refinery is estimated to be 6000 t/y.

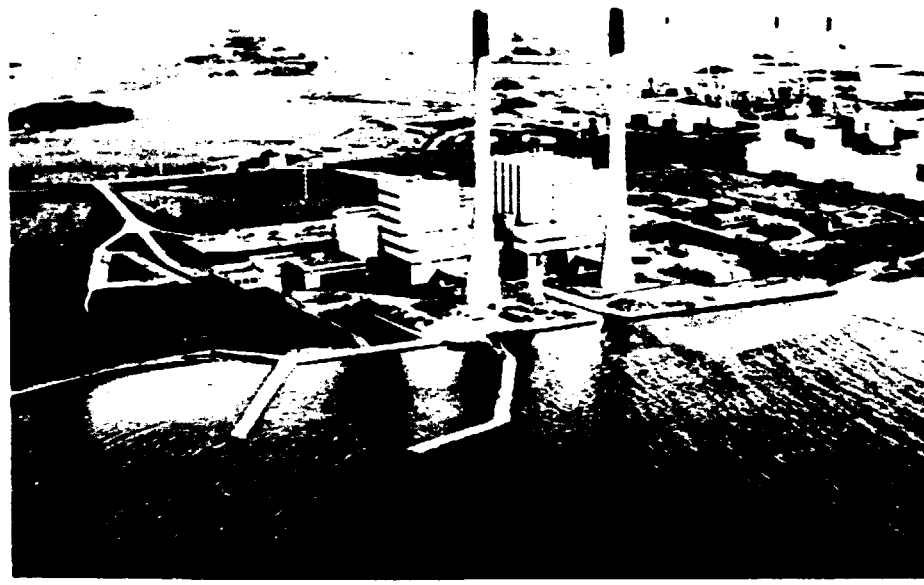

Fig. 1. The power plant at Stigsnæs on the south-west coast of Zealand. The Gulf Refinery is seen in the background.

A more detailed description of the power plant with lay-outs, diagrams, etc., can be found in leaflets published by SEAS* ("Stigsnæsværket", "Stigsnæsværket blok 2", no dates). The sulphur dioxide immissions in the surroundings of the plant were measured in 1972-73 (DEF 1975) and found to be typically 10 $\mu g/m^3$ for half-hour averages.

*Sydsjællands Elektricitets Aktieselskab - the South Zealand Electric Power Company

2. TRACER TECHNIQUES

As already mentioned, two tracers must be used to clarify the fate of sulphur dioxide. One is used to monitor the dispersion of the plume as such and must therefore be chemically inert - for this purpose sulphur hexafluoride (SF_6) was chosen. The other tracer is used to monitor the reactions of sulphur, and therefore a radioactive sulphur isotope (^{35}S) is the obvious choice.

In order to match the concentration of the tracers with the sensitivity of the instruments, the dispersion in the plume must be estimated. Our calculations are based on Turner's treatment of the diffusion theory (Turner 1970) assuming the meteorological conditions characteristic for Pasquill's stability classes A-F (Pasquill 1961 and references therein). As wind velocities for every stability class, typical wind velocities for Denmark were chosen. Results for distances greater than a few km are only rough estimates.

2.1. Sulphur hexafluoride, SF_6

Sulphur hexafluoride has proved to be a useful tracer for following air masses in dispersion studies because of its chemical stability in the presence of other atmospheric pollutants and sunlight, and its normally low background concentration in the atmosphere.

For power-plant plumes and similar emissions, an estimated release rate of SF_6 is 60 to 120 l/min ($\sim$ 22-44 kg/h) for experiments running for several hours per day. Typical power plants emit flue gas at a rate of 30 to 100 million l/min. The initial concentration of SF_6 in the stack would thus be of the order of 0.5 to $5 \cdot 10^{-6}$ parts/part (0.5 to 5 ppm). At about 5 km downwind inside the plume, on a representative run, atmospheric dilution will typically reduce this to 0.5 to $5 \cdot 10^{-10}$ parts/part, and at about 25 km downwind it will be reduced by another order of magnitude. Thus, SF_6 concentrations had to be determined with reasonable accuracy down to at least 10^{-12} parts/part in our studies. This was accomplished by means of special equipment developed by E. Lund Thomsen based on an idea of J.E. Lovelock (Lund Thomsen

and Lovelock 1976); this is described in greater detail in sect. 3.1.

2.2. Radioactive sulphur, ^{35}S

Sulphur-35 has been used as a tracer in many studies of SO_2, e.g. in laboratory experiments on photochemical oxidation (Cox and Penkett 1975) and in investigations of the velocity of deposition on different surfaces (Owers and Powell 1974).

Since ^{35}S has a half-life of 87 days and is a pure β-emitter, it is well suited for field studies and its use has been proposed for studies of long-range transport of atmospheric sulphur (Bergström et al. 1972). Although only pilot experiments were performed by this author, it appeared that the release of 1-10 Ci should allow determination of the ratio between the SO_2 and sulphate concentrations at distances up to 100 km from the stack. It was shown that, even when assuming very unfavourable weather conditions, etc., one experiment would at most give an individual radiation dose of 1/10 000th of that found permissible by the International Commission on Radiological Protection.

At Risø, ^{35}S can be produced by irradiation of amorphous sulphur in a thermal neutron flux at about $2 \cdot 10^{13}$ neutrons/cm^2·s. It has been shown that the ^{35}S is produced in a form free of other radioactive isotopes and that batches of up to 8 Ci can be delivered every second month. We had planned to release 8 Ci ^{35}S over one hour in each experiment. The ^{35}S was to be dissolved in CS_2 and added to fuel-oil on its way to a burner. In practice, the equipment shown on fig. 2 would have been used. For safety reasons, the equipment was mounted on two transport vans; the first contained a pressure flask with nitrogen, a container for CS_2 and the entire pump system; the second van carried a 3.5 l flask with the $^{35}S/CS_2$ solution placed in a 50 l steel container filled with shock-absorbing material. This material absorbs the solution should the flask break.

The principle of the system appears from the diagram on fig. 3. During operation, the $^{35}S/CS_2$ solution was to be pumped to a small burner used for lighting at the power plant; the in-

jection velocity could be adjusted by valves and pump gear and measured by a flowmeter. After operation, the entire system could be flushed with CS_2 to remove residual activity.

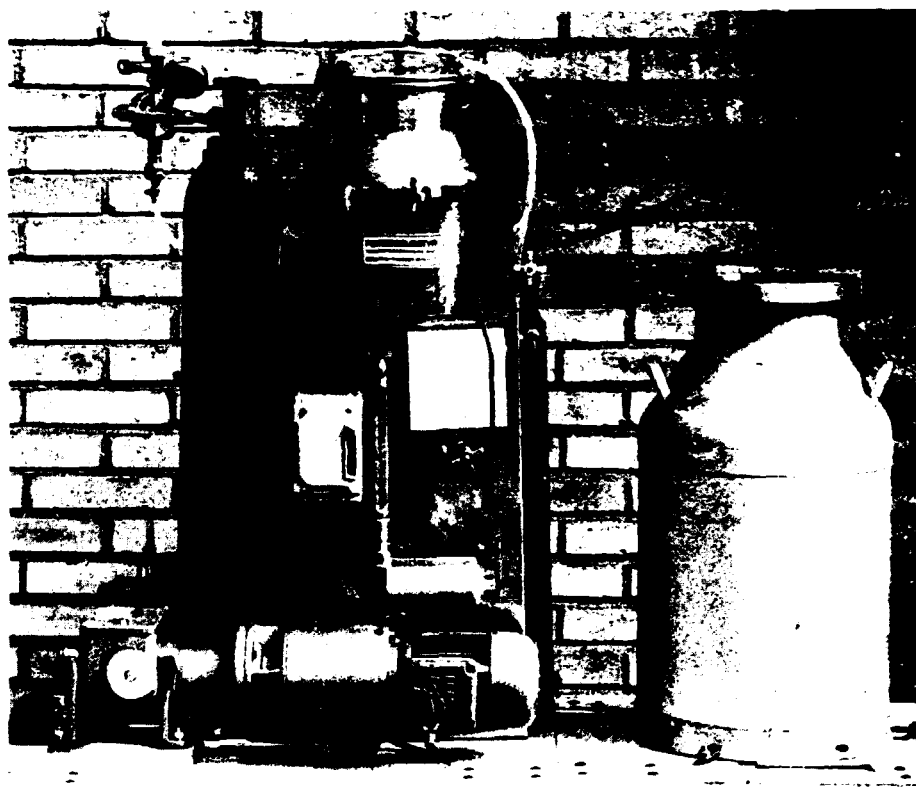

Fig. 2. The equipment for injection of ^{35}S. For safety reasons, the container with ^{35}S is placed in a separate van that can be rapidly removed in case of emergency.

The ^{35}S activity of SO_2 and sulphate would have been determined by collection of filter samples as described in sect. 3.7. One set of filters was to be used for each traverse and the collected activities could therefore be integrals of the concentrations in the horizontal direction. In order to estimate the accuracy of the subsequent chemical analysis (cf. sect. 4.2), we calculated the activities of ^{35}S which could be expected on the filters.

Typically, the weather in Denmark corresponds to Pasquill

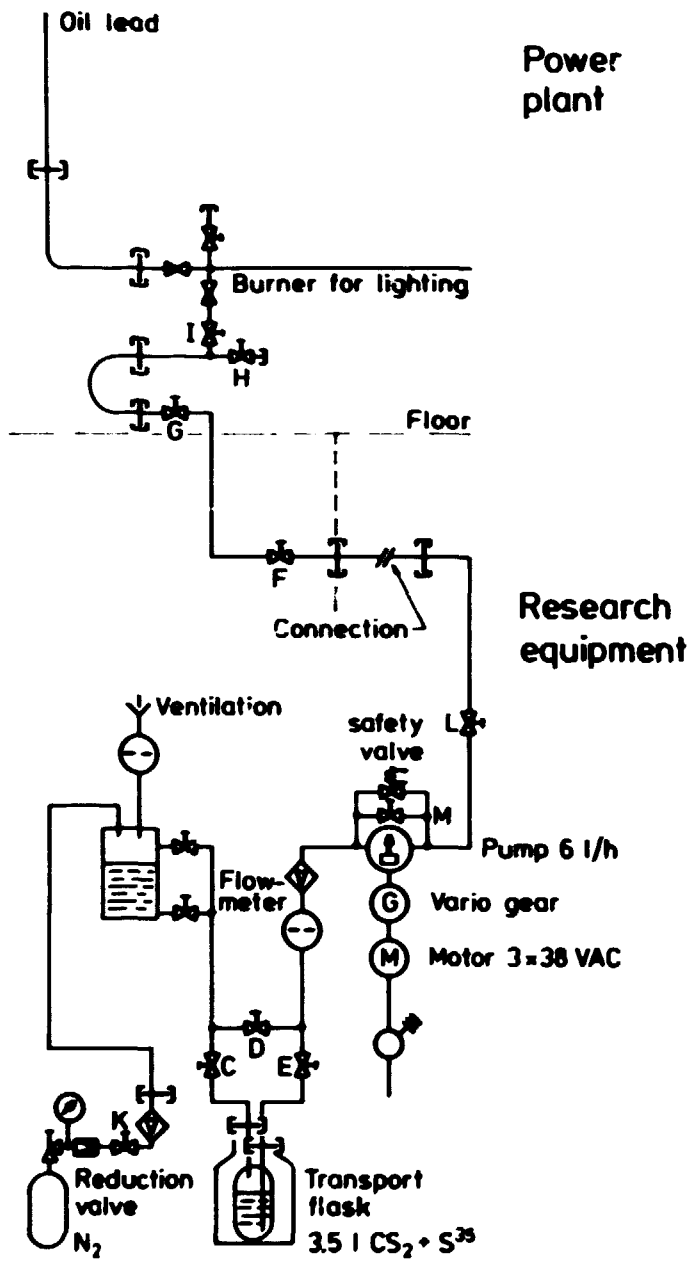

Fig. 3. Diagram of the pump system for injection of ^{35}S into a combustion chamber at the power plant. The research equipment is connected to the power plant through "connection". A photograph of the special research equipment (lower part of the diagram) is shown as fig. 2.

class D (60% of the time) with a wind velocity of 5 m/s. With the described equipment the total collected activity for one traverse would, under these circumstances, be $6 \cdot 10^{-11}$, $4 \cdot 10^{-11}$ and $3 \cdot 10^{-11}$ Ci at distances of 5, 20 and 50 km, respectively. Assuming that 10% of the sulphur was present as sulphate, 2-3 traverses would be necessary to secure a sample that could be analyzed with sufficient accuracy. More detailed results of these calculations will be published elsewhere (Lewin 1977).

3. AIRBORNE INSTRUMENTATION

The total weight of the instrumentation for the airborne measurements is about 700 kg and the electric energy consumption 1500 VA. This called for a fairly large aircraft, but at the same time, it was necessary to be able to fly slowly at low altitude. It was therefore decided to use an aircraft of the C-47 type (fig. 4), which is the military version of the DC-3. This aircraft was kindly made available by the Danish Air Force for the individual experiments. The aircraft was also used for other purposes, and it was not possible to borrow the same machine every time; thus the instruments had to be easily mountable and removable.

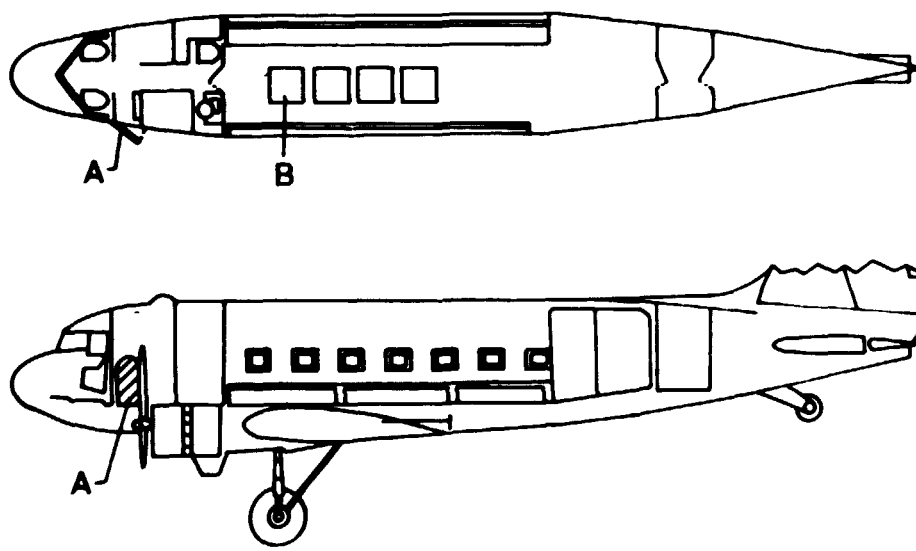

Fig. 4. The C-47 aircraft used for the airborne measurements. The intake system is placed on a cockpit door (A). The position of the instrument racks is shown by squares (B).

The intake system was mounted on a door which replaced the ordinary door on the side of the cockpit in front of the propel-

lers; fig. 5 shows the system schematically; it comprised a series of nickel-plated brass tubes of different diameters dimensioned for isokinetic sampling. All tubes were electrically heated in order to prevent ice and dew formation. Tubes for collection of sulphur compounds were coated with teflon on the inside. The temperatures were controlled by means of thermocouples.

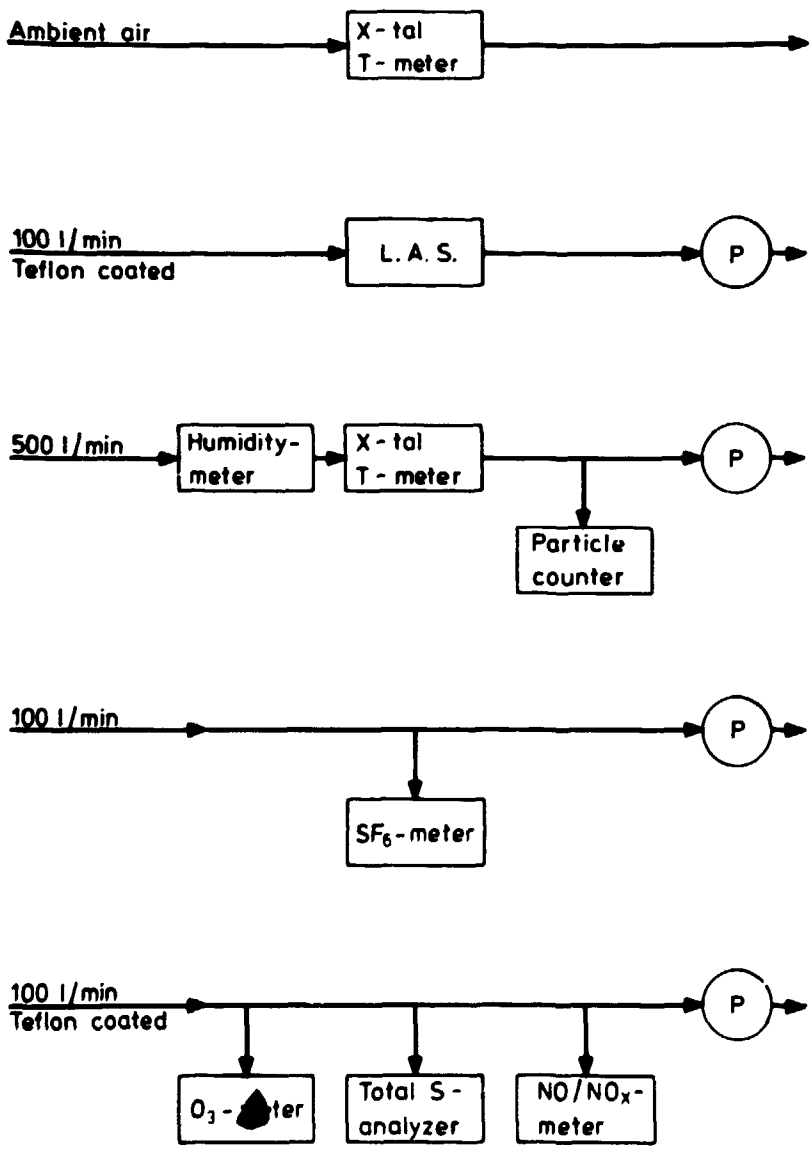

Fig. 5. Diagram of the sample-intake system located on the cockpit door. Besides the air pumps, P, most instruments have their own pumps.

Figure 6 shows the instruments in racks which were mounted in the aircraft as shown on fig. 4. Directly on the inside of the door is a filter-paper apparatus intended for collection of radioactive sulphate samples on untreated Whatman 41 paper and SO_2 samples on paper impregnated with a solution of KOH. These filters were later analyzed in the laboratory (cf. chapter 4). The rack-mounted equipment recorded the concentrations of ozone, nitrogen oxides and sulphur dioxide; in addition, ambient temperature and humidity were monitored. Figure 6 also shows a five-stage impactor intended for size-fractionated particle collection (cf. sect. 3.8). One of the most important instruments (not shown) is a system for continuous registration of SF_6-concentration (cf. sect. 3.1).

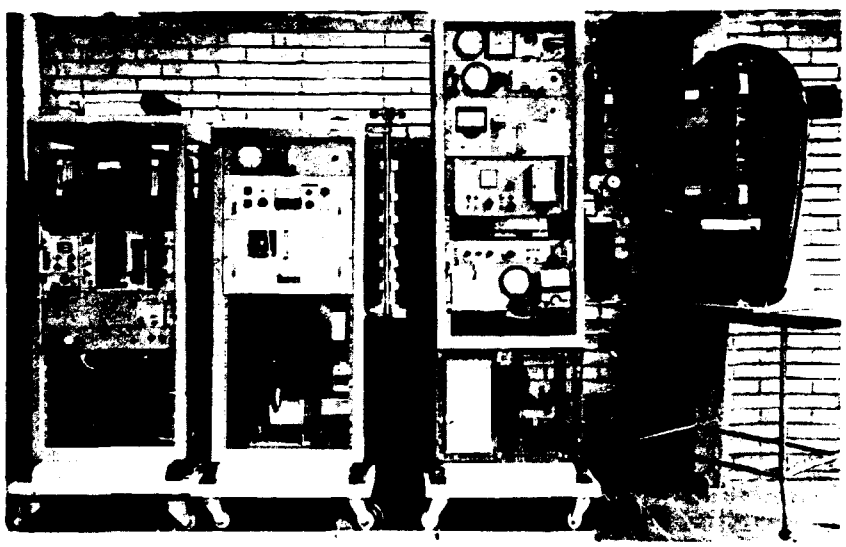

Fig. 6. The airborne equipment before installation. To the right is seen the cockpit door with sampling intakes and filter paper collectors for sulphur dioxide and sulphate samples (see also fig. 13). The SF_6-detector is not shown.

3.1. Sulphur hexafluoride meter

In airborne plume dispersion experiments using sulphur hexafluoride as a tracer, the electron capture gas chromatograph seems so far to be the only suitable instrument on account of the extreme sensitivity required of about 10^{-12} parts by volume.

If the gas chromatograph is used in the frontal mode (Dietz and Cote 1976), measurements of SF_6 are possible in the interval between the arrival of the sulphur hexafluoride frontal and the oxygen frontal at the detector. After this interval the measurement must be discontinued, because of the need to backflush the column in order to remove the oxygen, and after backflushing some time is necessary to equilibrate the column pressure.

A measurement interval of 3 1/2 minutes can be obtained when using a c. 5 m long molecular sieve column (Dietz and Cote 1976). However, this interval is followed by a period of about 10 min in which SF_6 cannot be recorded. This method has several fundamental drawbacks regarding its use in airborne plume measurements. On account of the limited measurement interval, the localization of the plume will be a hit-or-miss procedure resulting in a severe loss of the total experimental time normally available for performing the number of crosswind traverses necessary to determine the plume dispersion pattern up to, e.g., a distance of 30-300 km from the source. The available experimental time is typically limited to 5-6 hours. A no less important loss of measurement time is represented by the backflush intervals.

Hence, use of the conventional gas chromatograph is inappropriate for airborne plume experiments. There is need for continuous operation of the electron capture detector, which means that this instrument must be used without the column. The main obstacle to continuous measurement of trace concentrations of sulphur hexafluoride in the atmosphere using an electron capture detector is presented by the oxygen concentration, which must be reduced to the ppm range before sulphur hexafluoride can be measured with the required sensitivity. Lund Thomsen and Lovelock (1976) have constructed a device for this purpose, which utilizes the catalytic reaction of oxygen and hydrogen on a palladium surface, and mainly consists of a thin palladium tube surrounded by

an outer tube of copper. The system (shown schematically in fig. 7) is heated electrically to about 250°C. The sample air is led through the palladium tube, and hydrogen is admitted to the outer copper tube and permeates to the inner surface of the palladium tube, where the reaction takes place. The resulting water vapour is liquified in a heat exchanger and the water removed by means of a filter. The excess hydrogen from the reaction is removed by a second, heated palladium tube.

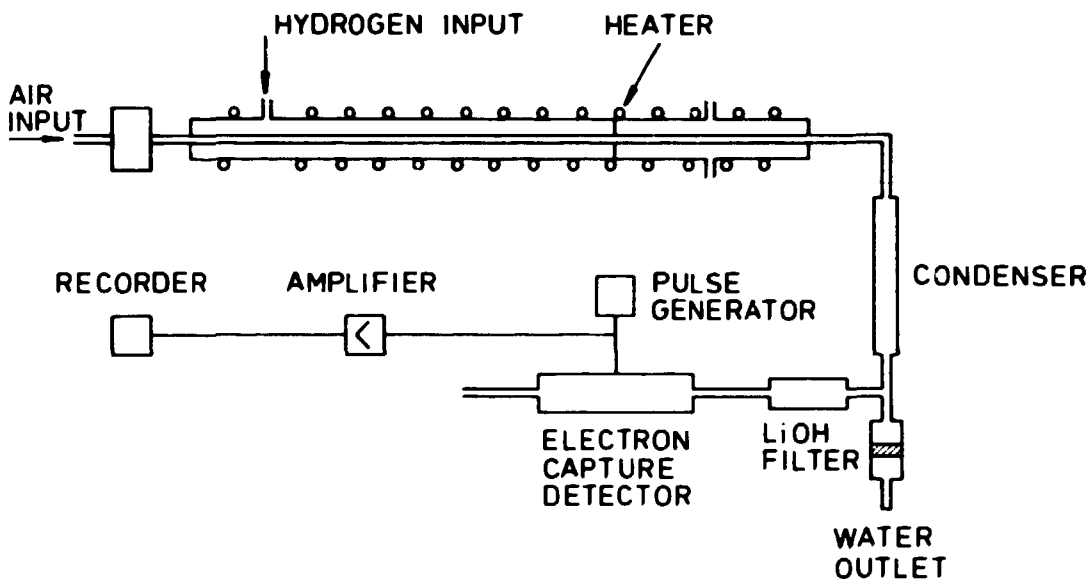

Fig. 7. Principle of the system for continuous registration of SF_6.

Having eliminated the selective element of the conventional gas chromatographic system, i.e. the column, the question arises of the interfering electron-capturing trace compounds in the atmosphere, e.g. the chlorofluorocarbons and the chlorocarbons. Here again advantage is taken of the catalytic reaction of these compounds with hydrogen on the palladium surface, where they are converted to electron transparent species (Lovelock et al. 1970). During the practical airborne test of the instrument, several traverses were made through the plume at a short distance from the stacks before the injection of SF_6 in order to test for interference. No signals were observed.

It is well known that calibration is extremely difficult for the very low concentrations involved. Different methods were used for preparing test solutions, e.g. the exponential dilution method, but they were found at best inconvenient. To overcome this problem, the electron capture detector was constructed for coulometric detection of sulphur hexafluoride. On account of its special geometry - cylindrical form and length about ten times that of the diameter - the ionization of SF_6 is complete within a few per cent for concentrations less than $5 \cdot 10^{-10}$ cm^3/cm^3, thus making it possible to calculate the SF_6 concentration detected directly from the area of the recorder response curve. The uncertainty is estimated to be about 10%, and the short-time reproducibility is about 2%.

The pulses for the electron capture detector are provided by a crystal-stabilized pulse generator, and the signal is amplified by means of an operational amplifier. The performance of the system is illustrated in fig. 8 which shows SF_6 plume profiles recorded during a practical airborne test.

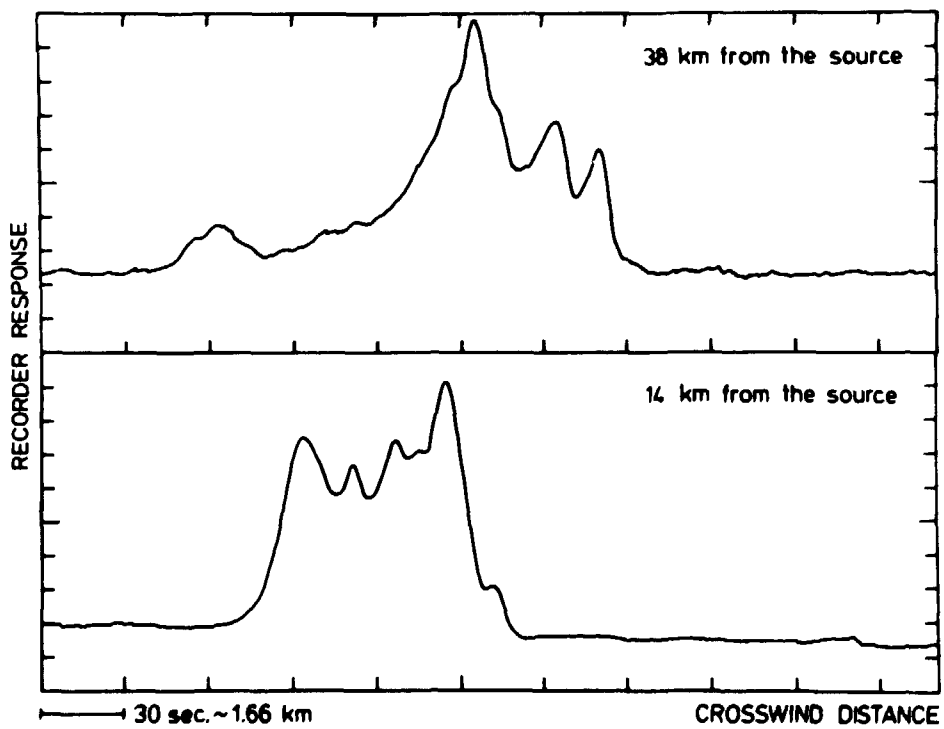

Fig. 8. Typical plume profiles recorded with the SF_6-meter.

3.2. Total sulphur monitor

The total gaseous sulphur in the air was monitored by means of a "Bendix" (type 8100) flame spectrophotometer. Operation is based on the detection of the emission from excited sulphur originating from sulphur compounds burnt in a hydrogen-air flame; the light intensity is proportional to the square of the sulphur concentration. Interferences from the flame emission produced by other elements are eliminated by arranging a photomultiplier tube viewing a small region above the flame through a narrow-band optical filter (fig. 9). The hydrogen and air are burned in an open tubing that shields the flame from the direct view of the photomultiplier tube. When sulphur is present emission occurs above the shielded flame, and the light is transmitted directly through the optical filter to the photomultiplier tube. When compounds not containing sulphur are burned, the flame emission takes place inside the hollow burner tubing and is thus shielded from the photomultiplier tube.

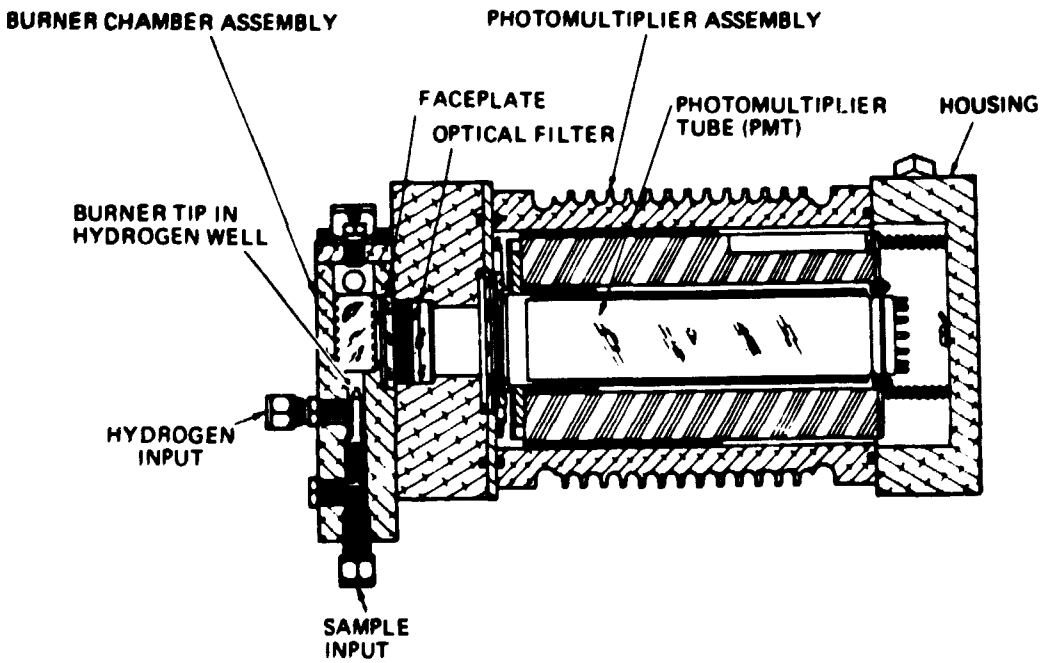

Fig. 9. Cut through the detection unit of the total sulphur monitor (from instruction manual).

It is obvious that this detector is extremely sensitive to changes in the flame height, which again depends on the sample air flow and hydrogen flow to the reaction chamber. The response as a function of flame height is demonstrated in fig. 10 that shows calibration curves of the instrument for two temperatures in the reaction chamber, which in turn are functions of flame height.

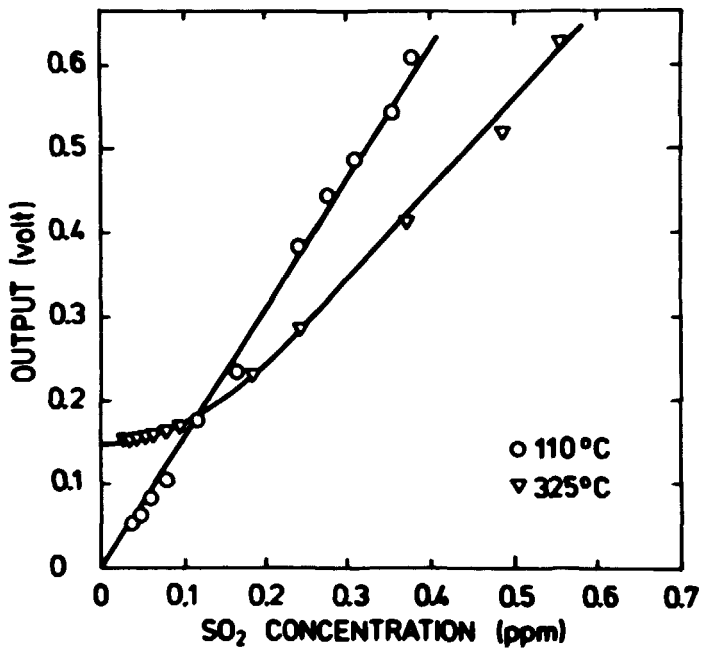

Fig. 10. Calibration curves for the total sulphur monitor for two different temperatures in the reaction chamber.

The instrument was calibrated with a permeation tube system and the temperature in the reaction chamber was measured by a thermoelement. The optimal reading was found to be at 110°C. For other temperatures, the calibration curve crossed the axis. Before beginning each traverse the flow to the reaction chamber was manually regulated to give this temperature. The flying speed under the traverse was kept constant and hence the air sample flow did not vary.

The influence of the tube material and length on the registered SO_2-level was investigated, and teflon was found to be suitable for SO_2-sampling. The monitored SO_2-level was constant and independent of the length of the teflon tubes up to at least 4 m. The delay time of the instrument in the laboratory set-up similar to that used during plume experiments was 6 s.

3.3. NO, NO_x-monitor

Concentrations of nitrogen oxides in the ambient air were continuously monitored by means of a commercial instrument (Thermo Electron Model 14). This provides at the same time information about plume profiles, and the instrument could thus be used for plume tracing. As the analytical principle, the reaction between NO and O_3 was utilized:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu \ .$$

The resulting chemoluminescence was monitored by a high sensitivity photomultiplier positioned at one end of a reactor, where the gas sample to be analyzed was mixed with O_3. A narrow band optical filter excluded any interferences. Since the light intensity is directly proportional to the NO-concentration, the electrical output signal from the photomultiplier is the direct measure of gas concentration.

To measure NO_x-concentration ($NO_x = NO + NO_2$), the sample gas flow is directed through an NO_2-to-NO-converter based on thermal reduction on a metal surface. The instrument operates automatically or manually. In the automatic mode, NO and NO_x are registered alternately; in the manual mode, only the selected gas is monitored. In the automatic mode the switching time is about 50 s, this makes the instrument unsuitable for airborne measurements. In the manual mode the time constant is much lower but still too large to give a reasonable resolution of the plume. Fortunately, however, it was possible to modify the instrument to meet the requirements of airborne experiments simply by extracting the signal just after the preamplifier. With the instrument working in this way, and in a set-up as used in the aircraft, the response time ($\sim$ 60% of full signal) was 3.6 s.

In an attempt to further reduce response time, the signal from the photomultiplier was directly extracted, amplified in an electrometer (Keithley Instruments, Solid State electrometer, model 602), passed through an adjustable RC-circuit and recorded. In this set-up the overall response time could be as low as 0.5 s. Normally, the RC-circuit was adjusted to give a signal-to-noise ratio of about 10 corresponding to a response time of 1.4 s.

A system for the dynamic calibration of the instrument (O'Keeffe and Ortman 1966) was set up which was based on a permeation tube (Lindquist and Lauting 1972) made of glass with a teflon cap and partly filled with nitrogen dioxide. For constant temperature, the permeation rate of nitrogen dioxide through teflon is constant and can be measured by weighing. The output from the tube is led to a mixing chamber under constant flow, where it is further diluted.

The system was used for calibration of the nitrogen oxide-analyzer in the range $5 \cdot 10^{-3}$ - 10 ppm of NO. The result is shown in fig. 11.

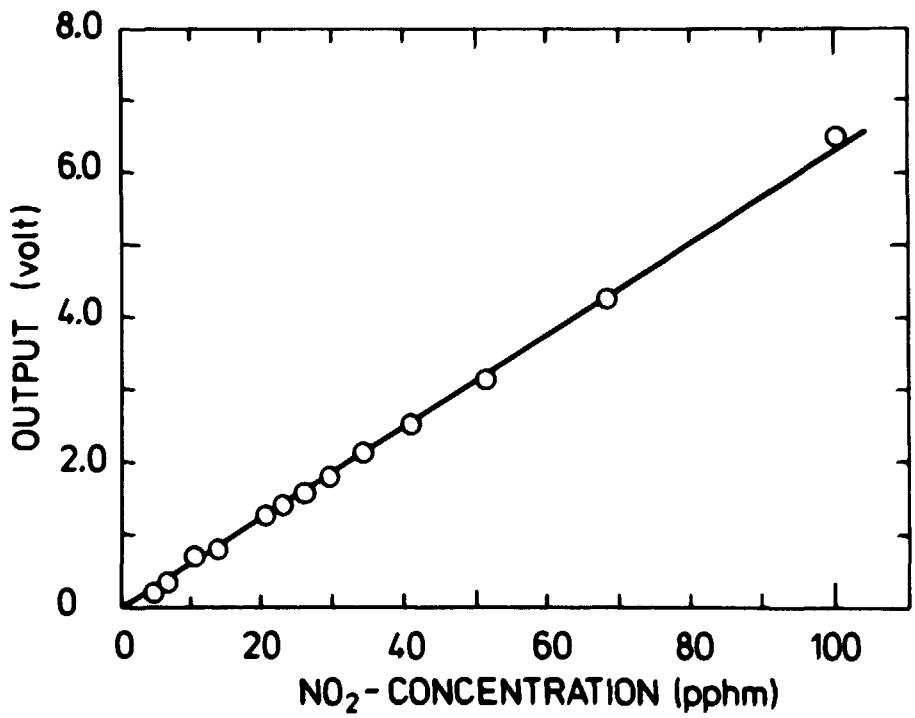

Fig. 11. Calibration curve for the NO_x-meter.

3.4. Ozone-meter

An ozonemeter based on the chemoluminescent reaction between ozone and ethylene was constructed at Risø. It is shown schematically in fig. 12. The air containing ozone and the ethylene are mixed in front of a photomultiplier. Typical flows are 1 l/min of air and 20 ml/min of ethylene. The sensitivity is about 5 ppb and the signal is linear with respect to ozone concentration up to about 2 ppm. The reaction is fast and there is no interference from NO_2 and SO_2. The signal from the photomultiplier is passed to an analogue-to-pulse converter and registered by a count-rate meter.

Calibration has temporarily been based on the KJ method (Saltzmann and Gilbert 1953). Later we intend to use the more convenient photometrical calibration based on the absorption of 253.7 nm radiation in O_3.

The instrument is described in greater detail in a separate report (Lund Thomsen, to be published).

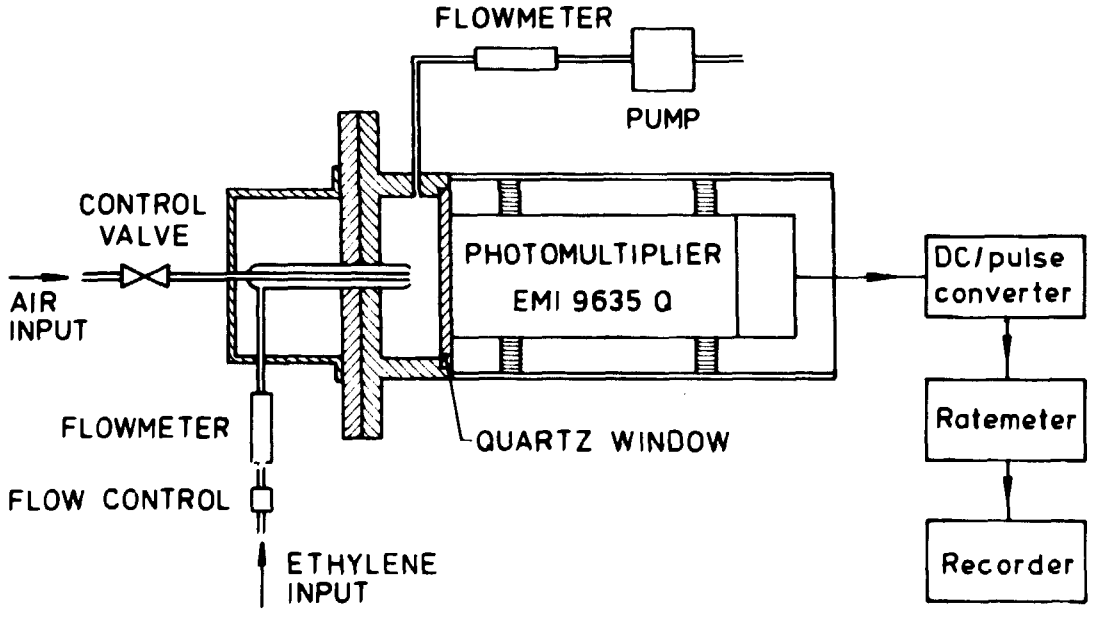

Fig. 12. Principle of the ozone meter.

3.5. Particle counter

A commercial particle counter (Environmental One Cooperation, type Rich-100) was used for measurements of plume profiles and particle concentrations. The instrument is designed for real-time detection and measurements of submicron particles and operates on the principle of a cloud chamber. A constant flow air sample is periodically diverted through a humidifier and then into a cloud chamber, where an expansion of the sample occurs, producing a cloud. The attenuation of light by the cloud is measured and used to produce a signal that is proportional to the condensation nuclei concentration. After expansion, the cloud chamber is pressurized and flushed out. The total measurement cycle-time is approx. 1 s.

The instrument has no measurable delay time and the response time is 7.2 s. The measuring ranges cover 500-300 000 particles/cm^3, but the response can be slightly non-linear in the highest range.

3.6. Temperature and humidity meters

The temperature was measured outside the aircraft and just prior to the humidity meter by means of a commercial instrument (Hewlett-Packard, Model 2801A), in which measurement is based on determination of the frequency difference between two precision oscillators, one of which is thermostated and the other exposed to the air. The manufacturer claims a calibration accuracy of $0.02^{o}C$.

The relative humidity was likewise measured by means of a commercial instrument (Vaisala H.M. 11), in which measurement is based on the determination of the capacitance change with humidity of a thin-film capacitor filled with a dielectric polymer.

3.7. Low-volume air sampler

Particulate sulphate and gaseous sulphur dioxide samples for subsequent laboratory analysis (cf. ch. 4) were collected by means of a low-volume air sampler (LAS) constructed at Risø; it is shown on fig. 13.

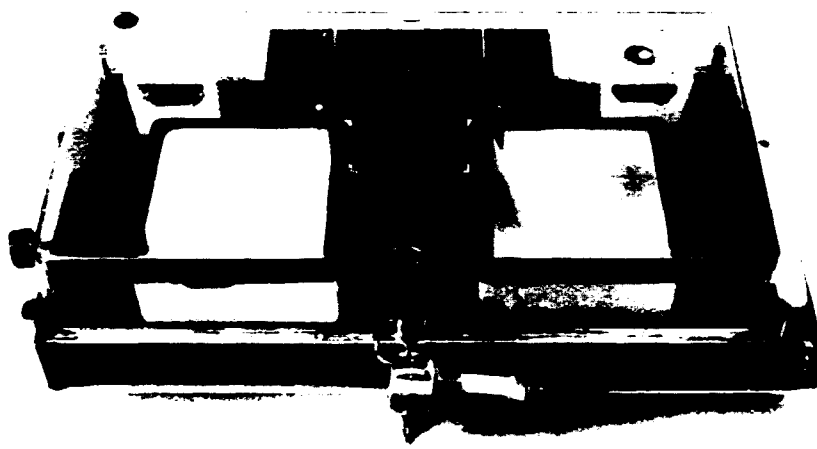

Fig. 13. Close-up of the low-volume air sampler (LAS). During measurements the sampler is placed on the inside of the cockpit door, as shown in fig. 6.

The air is first passed through an untreated Whatman 41 filter paper, which collects particles, and then through a similar filter impregnated with 0.5 N KOH (cf. fig. 13), which retains sulphur dioxide. The technique applied for sampling the sulphur dioxide was first described by Huygen (1962), who used a filter paper with a low sulphur content impregnated with a solution of 25% potassium carbonate and 10% glycerol in water. Instead of this very strong alkali solution, we used 0.5 N KOH. The amount of absorbing material was sufficient for the amounts of SO_2 collected, and the sulphur content of the filter proper was much lower. The apparatus for impregnation is shown in fig. 14.

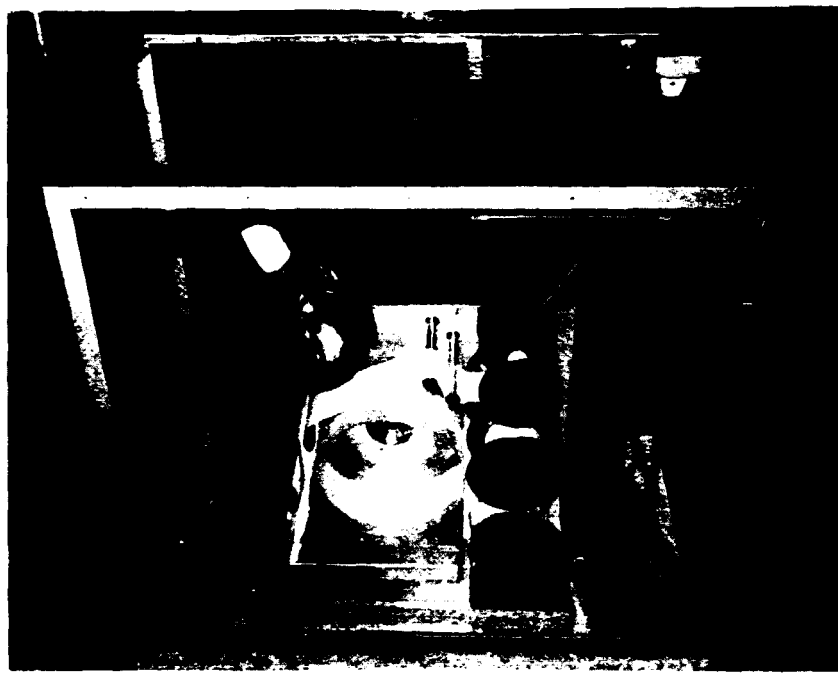

Fig. 14. The apparatus for impregnation of filter strips for the low-volume air sampler (cf. fig. 13). The strips are automatically passed through a KOH-bath (0.5 N) and dried under an infrared lamp.

The filters are in the form of rolls, contained in closed magazines and transported manually to the exposure aperture. During exposure, the filters are clamped airtight into holders. After exposure, the exposed area is marked and the strip moved one step forward. The filter strips are collected in closed chambers and subsequently the exposed areas are cut out and analyzed. The filter-carrying cylinders in the drive mechanism are teflon-coated. The air-flow through the filters is measured on a flow-meter placed downstream of the filters and regulated by a pump-valve. Flow readings are corrected for the pressure drop through the filters and for flying speed.

3.8. Cascade impactor

A five-stage impactor was developed for separation of particulate matter in the air samples into size fractions (Wåhlin and Heidam 1976). The design ensures that the air streams in the nozzles are laminar, thus preventing losses of particles on the nozzle walls. The jet orifices are rectangular, and the individual fractions are collected on impaction plates covered by a polystyrene film.

The calculation of the cut-off diameters for a specific volume flow rate is based on a refined impactor theory which takes the boundary layers on the nozzle walls and the impaction plates into account. These calculations require a measurement of the pressure drop over the nozzles. The theory makes it possible to determine the smallest aerodynamic diameter for which a particle will be collected on a specific impactor stage at a given volume flow rate.

In the actual separations, the exposed polystyrene films are transferred to target frames and analyzed by proton-induced X-ray fluorescence. So far, however, this instrument has only been tried a few times during airborne experiments because the volume of sample obtained in only a few traverses was too small.

4. CHEMICAL ANALYSIS

The activity of sulphate and sulphur dioxide was to be measured by collection on filters (cf. sect. 3.7) which would have been subsequently analyzed in the laboratory. One filter was to be used for each position and the collected activity would therefore have been a measure of the integral of the horizontal concentration profile.

The filters can also be used for determination of inactive sulphur compounds, which are then extracted in water. The inactive sulphur is determined by isotope dilution technique. This involves the addition of ^{35}S, but the amount of ^{35}S already present in the samples is negligible in this connection.

4.1. Analysis for ^{35}S tracer

As sulphur-35 is a pure β-emitter, counting must be performed with a liquid scintillation counter; Bray solution (Bray 1960) is used as scintillation liquid. Due to the background, only activities down to ca. $5 \cdot 10^{-12}$ Ci can be determined. If we assume that about 10% of the sulphur is in sulphate form, the collection of a sufficiently active sample thus requires several traverses (cf. sect. 2.2). The determination can be carried out in two ways:

1. The sample is extracted into a known volume of water and an aliquot of the extract is counted. No quenching effects from filter impregnation or other possible impurities have been observed. The counting efficiency is about 95%, established against the reference sample containing the same amount of radioactivity. The counting time for 1 μCi samples is 10 min, for 0.1 and 0.01 μCi it is 100 min. This method has the advantage that a further aliquot of the same extract can be used for analysis of inactive sulphur. At most, a 500 μl aliquot can be added to 5 ml scintillation solution; therefore the method is most suitable for relatively active samples as only a part of the collected radioactivity can be counted.

2. The filters are placed directly in the scintillation liquid and counted. Because of varying quenching in the filter paper, the counting efficiency is reduced to about 80% and the results scatter more. The activity of unimpregnated as well as impregnated filter paper blanks is practically zero. The manner in which the filters are placed in the scintillation vials does not affect the efficiency. The advantage of this method is that no chemical pretreatment is necessary and that the total sample can be counted. It is, on the other hand, a disadvantage that the method is destructive.

4.2. Analysis for inactive sulphur

The inactive sulphur is determined by a very sensitive isotopic dilution method developed by Klockow et al. (1974).

$Ba^{35}SO_4$ in an ammoniacal EDTA-solution is used as an isotopic dilution reagent. 100 µl $Ba^{35}SO_4$/EDTA solution is mixed with 500 µl sample solution and 500 µl ethanol. Sulphite from impregnated filters is oxidized to sulphate by adding a few drops of 30% H_2O_2. The pH is adjusted to 2-3 with hydrochloric acid, and Ba is thus precipitated as $BaSO_4$, leaving the excess of sulphate, corresponding to the amount from the sample, partly as $^{35}SO_4^{-2}$ in the supernatant liquid. To obtain coarse-grained precipitate, the sample is kept at 50°C for 20 hours. After separation, the activity of an aliquot of the supernatant liquid is measured by means of a liquid scintillation counter. Standard solutions are treated in the same way to produce a calibration curve for every series of samples. The amount of activity added is determined from the non-acidified sample, where no $BaSO_4$ is precipitated.

The amount of sulphur from a sample or a standard solution is:

$$x = \frac{A_x}{A_o - A_x} \cdot a$$

where A_x is the activity of supernatant liquid, A_o is the activity added, and a is the amount of sulphur in the ammonia/EDTA $Ba^{35}SO_4$ solution. Two solutions of isotopic dilution re-

agent with 14 µg $BaSO_4$/100 µl and 70 µg $BaSO_4$/100 µl, respectively, were used, corresponding to determination ranges of 0.1-2 µgS/ml and 0.5-10 µgS/ml. An example of a calibration curve is shown in fig. 15.

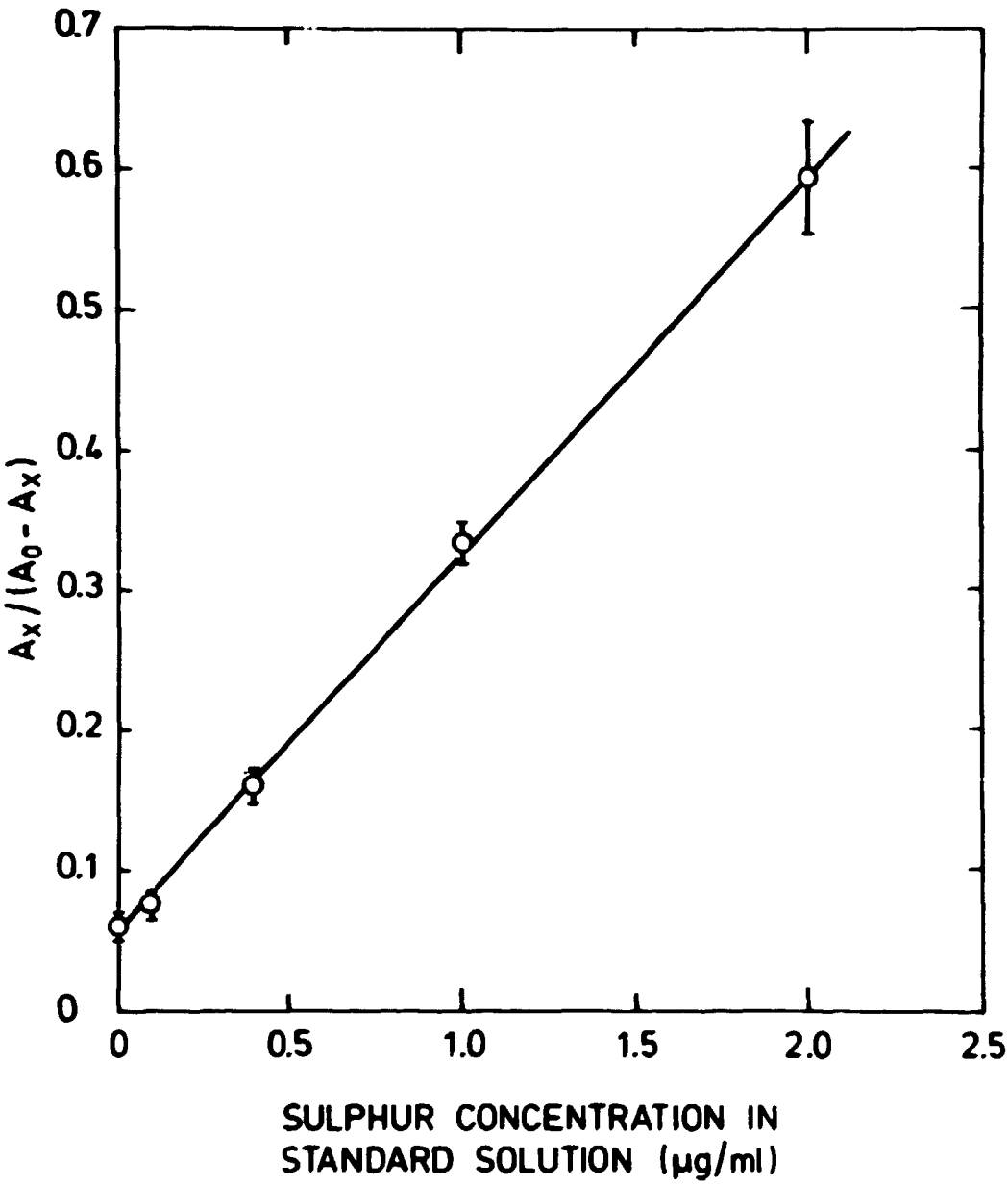

Fig. 15. Example of calibration in isotope-dilution analysis. Standard deviations are indicated.

Sulphur in particulate form collected on untreated cellulose filter paper can be determined in the same way after the extraction of the filter deposit into water. The determination can also be done directly on the filter by placing it in the mixture of $Ba^{35}SO_4$, water and alcohol and shaking it for some time. Hydrochloric acid is then added and the analysis is carried out as described before.

Gaseous sulphur samples, collected on filters impregnated with KOH, must be pretreated before the analysis. The average base content in impregnated filters is about 17 $\mu eq/cm^2$ and as the analysis is carried out at pH 2-3, the sample must first be neutralized. An ion exchanger in hydrogen form, e.g. Dowex-50 X, is used for this purpose. The resin is first washed with 0.1 N NaOH in order to remove sulphur impurities and then regenerated with an excess of 0.1 N HCl, followed by washing with distilled water. Finally, the excess water is removed by suction with a vacuum pump.

The filter to be analyzed is cut into small pieces and placed in a centrifuge tube. About 50-100 mg of the freshly washed ion-exchanger is added and the filter content is extracted to 2 ml of water by shaking the tubes for some minutes on a shaker. The pH of such prepared samples is about 4.5.

After centrifuging, 2 × 500 µl of the supernatant liquid are removed for duplicate analysis, which is carried out as described earlier. The accuracy of the method has been controlled for filter samples containing a known amount of sulphur.

Comparison of the results of analysis carried out at different laboratories with different methods showed that isotope dilution is the most accurate method for small amounts of sulphur (NILU, private communication, 1974).

4.3. Investigation of the effectivity of impregnated filters

Impregnated filter papers, used for the collection of SO_2, were investigated for their retention efficiency as function of linear velocity, SO_2-concentration, loading (fraction of impregnation used), relative humidity, and temperature.

Air containing known amounts of SO_2 was drawn through two impregnated filters in series. The relative humidity was varied by mixing measured streams of dried and wet air. The efficiency n of the filters was then determined from the quantities of sulphur dioxide, S_1 and S_2, found on the first and second filter, respectively:

$$n = 1 - \frac{S_2}{S_1} .$$

Investigations at temperatures lower than room temperature were carried out in a thermostated freezer.

The results show that the retention efficiency is above 90% provided that the crucial parameters are within the following ranges: face velocity 54-90 cm/s; loading 10-90%; SO_2-concentration 0.007-0.1 ppm, relative humidity 30-100%. No temperature effect was observed for temperatures in the range -10 - +25°C. This investigation is described in more detail elsewhere (Lewin and Zachau-Christiansen 1977).

5. AIRBORNE EXPERIMENTS

Many problems concerning meteorology, navigation and practical experimental planning had to be solved before the flights were carried out.

5.1. Meteorology

Weather conditions under which the flights could take place were limited mainly because safety considerations required a visibility of at least 8 km and a cloud base higher than 500 m. From the experimental point of view, weather requirements were a reasonably stationary wind field with respect to direction and velocity during the time of the flight.

Weather forecasts were received 72, 48 and 24 hours before a planned experiment. These forecasts were made by the Meteorological Section at Risø in collaboration with the Danish Meteorological Institute.

After an experiment, the meteorological conditions were described by means of data from radiosonde stations at Gothenburg, Copenhagen, and Slesvig, supported by data from meteorological tower installations near the Stigsnæs power plant and at Risø.

5.2. Navigation

In order to obtain a useful experimental determination of the plume pattern, it was necessary to correlate the data to a coordinate system with an error that was small compared to the smallest plume width (typically about 1000 m) observed.

This correlation was made by special use of the aircraft altimeter and the DECCA navigation system. At the beginning and end of a measurement run, e.g. a traverse flight through the plume, the instruments in question and a clock were photographed; marker pulses were simultaneously given to the instrument recorders. Further details regarding the practical use of this method are given in section 5.3. The coordinate errors are ±10 m for the altitude and about ±40 m for the two horizontal coordinates.

DECCA maps covering the operational area, in as much detail as consistent with these horizontal coordination errors, were computed and prepared by the Nautical Division of the Danish Water Board (fig. 16). The maps were constructed from existing sea level maps. A special problem in this connection was the refraction of the DECCA lines at larger obstacles and especially at the sea/land boundary. However, measurements performed by the Danish DECCA company showed that the effect was negligible for altitudes greater than about 100 m. Because the measurements were always carried out well above this altitude, the inherent precision of about ±40 m could be fully exploited.

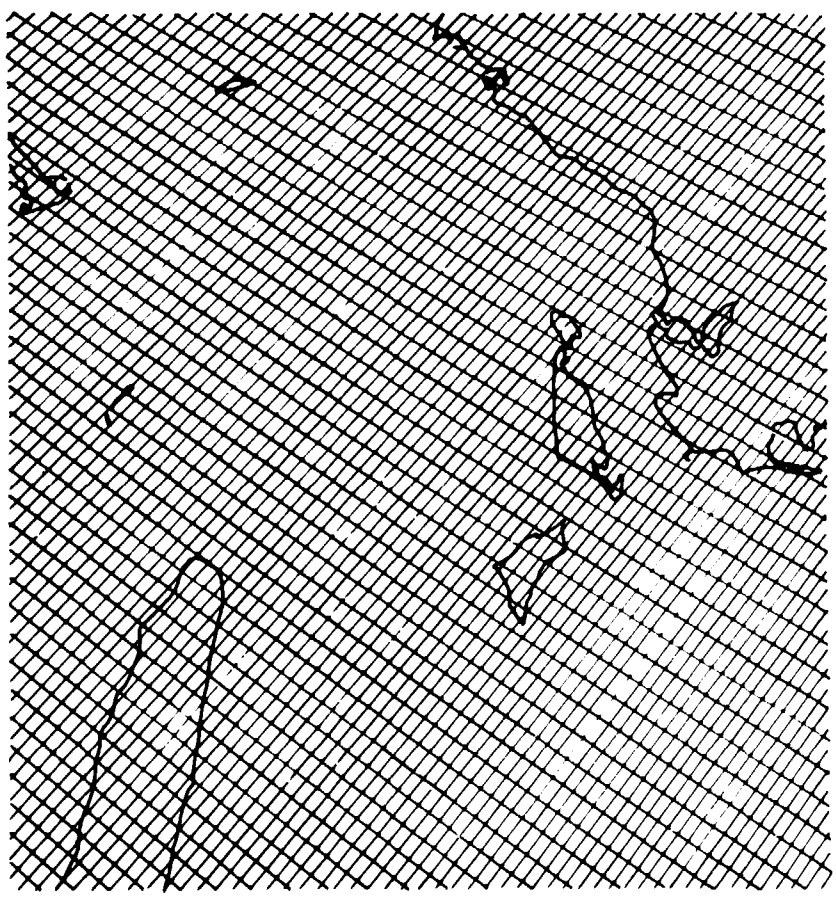

Fig. 16. Decca chart covering the surroundings of the Stigsnæs power plant, cf. figs. 18 and 19.

5.3. Practical plan of the experiment

Immediately before the start of an experiment the latest meteorological data relating to, i.a., atmospheric stability, wind vector distribution, altitude of cloud base, cloud and low-lying inversion, were collected. On the basis of this information, the Meteorological Section at Risø computer-calculated the position and dimension of the plume as defined by the effective stack height, h_{eff}, and the deviations, σ_y and σ_z as estimated by Turner (1970).

On arrival at the Stigsnæs power plant the wind-direction was determined by flying parallel to the visible part of the plume. Further, at least 3 traverses were performed at a distance of about 4 km from the plant in order to determine the actual height of the plume and to check the overall performance of the instruments.

Following this, an order was put through by radio to the power plant to inject the tracer. While waiting for a message from the plant giving the exact time of injection and while waiting for the tracer to reach a distance suitable for measurements in the plume, the background was measured for about 30 minutes by flying upwind.

When aircraft returned to the power plant, the actual plume measurements started. The method was as follows; at each chosen distance from the source, a number (3-5) of traverses were made perpendicular to the plume axis at different altitudes. The actual number was a compromise between the number of distances from the source that could be investigated during the operation time of about 6 hours and the possibility of obtaining good statistics for the measurements at each distance chosen.

An actual traverse flight was carried out as follows: guided by the estimate of the plume position described above, a "lane" was constructed on the map. The lane axis was identical with the plume axis and the lane borderlines were placed parallel to this axis at a distance ensuring that the plume was well inside the lane. From a holding position outside the lane, the aircraft was then directed towards the borderline on a course perpendicular to the plume axis at a speed of 200 km/h. At the first borderline, the DECCA instruments, altimeter clock and a counter were

photographed by polaroid camera; simultaneously, marker pulses were given to the various instrument recorders, followed by clock pulses keeping the time record during the traverse. At the second borderline, a second picture was taken. Figure 17 shows a typical photograph.

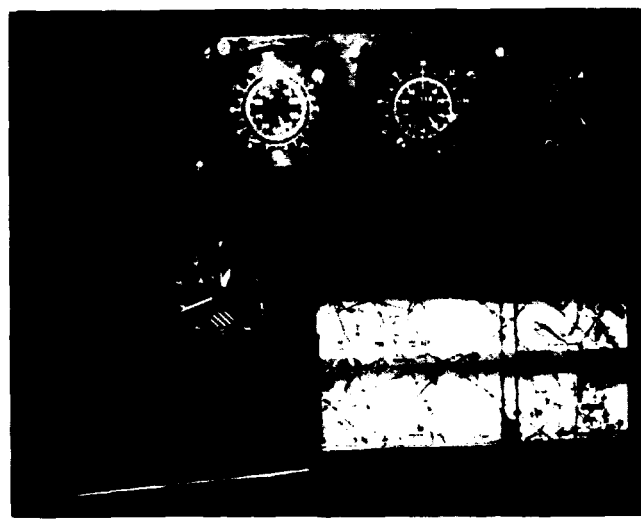

Fig. 17. The Decca navigation instrumentation. The photograph is a copy of a Polaroid picture taken during an experiment.

6. RESULTS

Nine flights were carried out around the Stigsnæs power plant. Five of these yielded proper results, the others were used to test the equipment only. Figure 18 shows the wind directions and the positions where the plume was crossed. Figure 19 shows the actual traverses for a single flight performed on 9 July 1975 (cf. sect. 6.3).

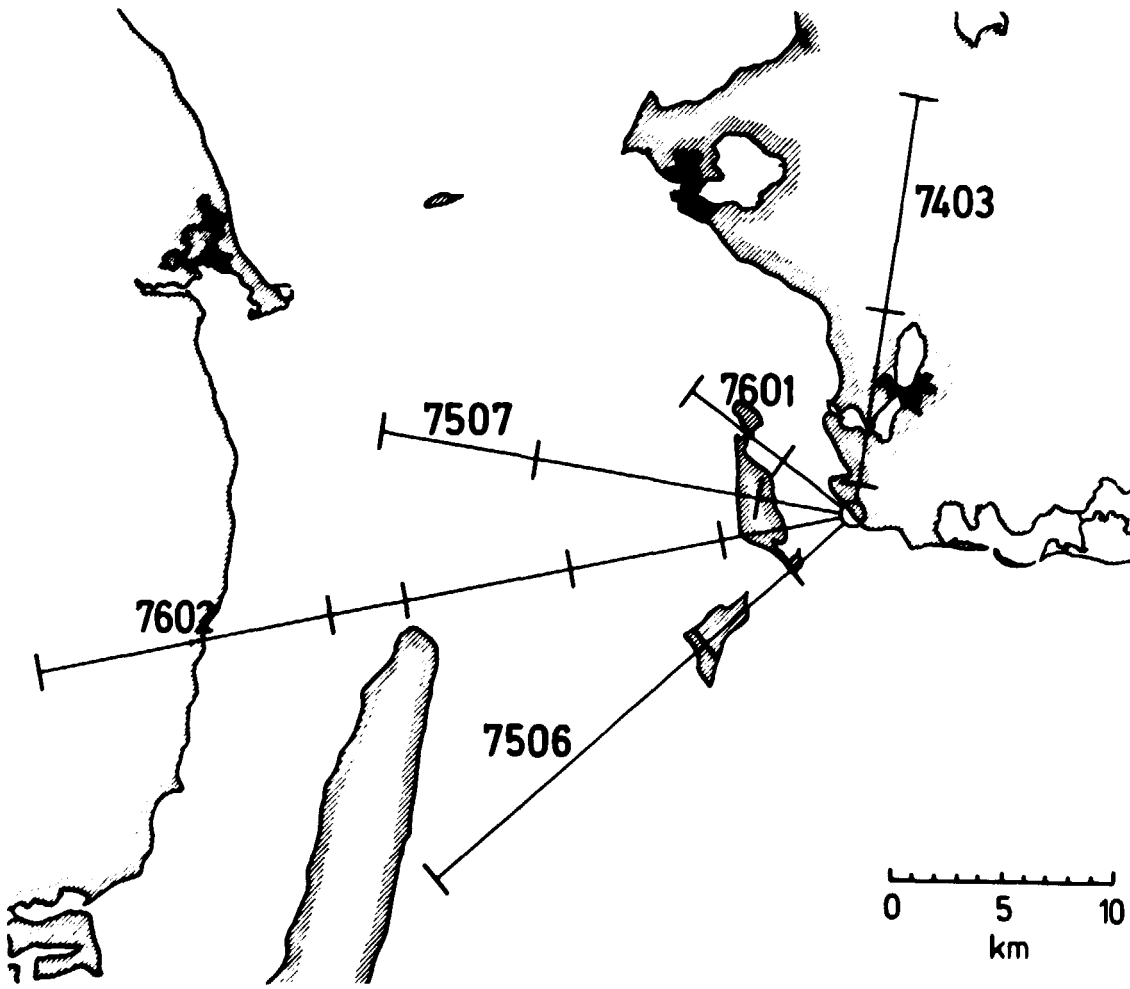

Fig. 18. Simplified map showing the surroundings of the Stigsnæs power plant with indication of wind directions and plume traverses for five flights (cf. sects. 6.1 - 6.5).

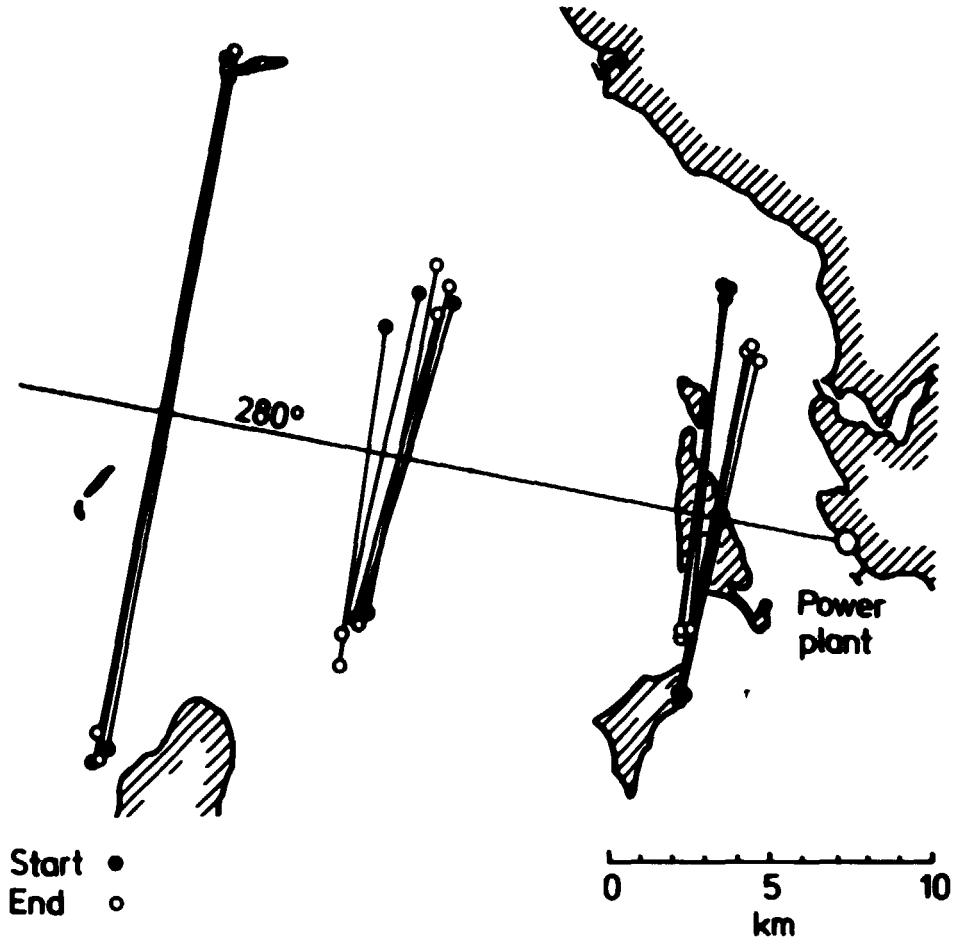

Fig. 19. Indication of traverses for a single experiment (9 July 1975).

6.1. Flight No. 7403; 18 October 1974

Weather: Radiosonde measurements at Jægersborg (near Copenhagen) indicated a cloud base at 600 m with neutral atmospheric stratification below. Wind direction SSW, with velocity about 3 m/s.

Airborne measurements and results: The plume was detected by means of the Bendix instrument (SO_2) at distances up to 18 km. All instrumentation (except the SF_6-monitor) was checked and it was found that various improvements were needed. The impactor could not collect sufficient material for analysis.

6.2. Flight No. 7506; 18 March 1975

Weather: The sky was partly overcast with cumulus clouds; the temperature was about 3°C; relative humidity about 70%, wind speed about 9 m/s. Wind direction NE. Radiosonde measurements at Jægersborg and Slesvig indicated neutral atmospheric stratification.

Power plant: Block 1 was running with a fuel consumption of 18 tons/h and block 2 with 50 tons/h; in both cases the sulphur content was 2.6%.

Airborne measurements and results: The experiment comprised tests of the same instruments as in flight No. 7403. Reasonable agreement between the SO_2, NO_x and particle monitors was found, but under the prevailing weather conditions it was difficult to detect the plume at distances greater than about 10 km. Results of sulphur analyses are shown in table 1. Results for 25 km distance are only tentative.

Table 1. Results of sulphate and sulphur-dioxide determinations on filter papers from flight No. 7506

Distance from power plant km	Sulphate concentration $\mu g/m^3$	SO_2 concentration $\mu g/m^3$	$\frac{[SO_4]}{[SO_2]}$
5	23.3	50.6	0.46
5	8.4	96.4	0.09
10	12.9	148.2	0.09
25	3.9	23.5	0.17
25	10.6	36.1	0.29

6.3. Flight No. 7507; 9 July 1975

Weather: The sky was cloudless; wind E-SE with velocity about 12 m/s; temperature about 18°C. Relative humidity 35%. Radiosonde measurements at Jægersborg gave the height of the lowest inversion layer at about 380 m; below the inversion the atmosphere was very unstable.

Power plant: Block 1 was shut down and block 2 was running at full power with a fuel consumption of 58 tons/h; sulphur content in the fuel 2.8%. For half an hour (1130-1200) the oxygen supply was slightly reduced, thus colouring the plume and facilitating tracing.

Airborne measurements: The measurements comprised SO_2, NO_x (or NO) and O_3-concentrations as well as the number of particles per cc. The plume was crossed at three distances from the stack: 4.3 (6 times), 14.5 (6 times) and 21.5 km (4 times) with a constant flying speed of 56 m/s. The centre line was found at a height of about 250 m.

Results: An attempt was made to use NO_x as an inner tracer for determination of SO_2 removal. Figure 20 shows the mean ratios of the integrated SO_2 and NO_x concentrations found by planimetry of the recorded curves. An analysis of the raw data shows that the ratio (y) decreases with distance from the source (x in km) according to the regression equation:

$$y = 3.86 - 0.12\ x\ .$$

The level of significance is 0.02.

The results of the analysis of inactive filter samples are given in table 2.

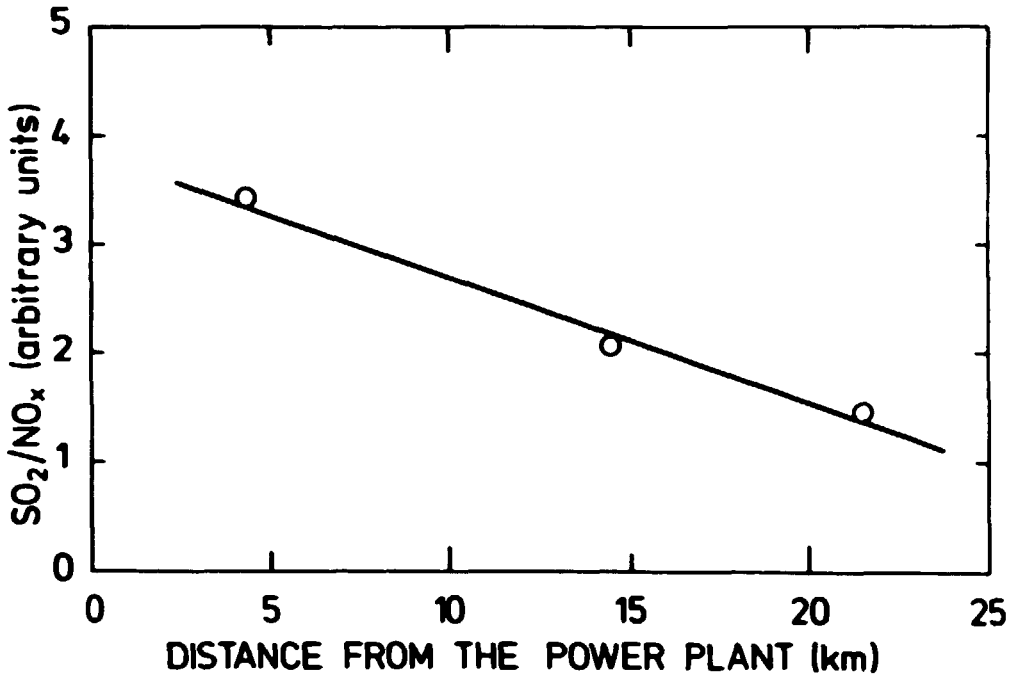

Fig. 20. The ratio between integrated SO_2 and NO_x concentrations determined from the traverses indicated on fig. 19.

Table 2. Results of sulphate and sulphur-dioxide determinations on filter papers from flight No. 7507

Distance from power plant km	Sulphate concentration $\mu g/m^3$	SO_2 concentration $\mu g/m^3$	$\frac{[SO_4]}{[SO_2]}$
4	22	142	0.15
15	20	102	0.20
22	0.6	209	0.03
30	0.5	260	0.02

6.4. Flight No. 7601; 4 March 1976

Weather: The sky was partly overcast with alto cumulus clouds having a base at a height of about 2.5 km; temperature 6°C. The stability in the flying area was neutral with low wind velocity (∿ 4 m/s), direction SE. Radiosonde measurements at Slesvig indicated an inversion of about 800 m.

Power plant: Block 1 was shut down and block 2 was running with a fuel consumption of 55.4 tons/h until 1400; it was then gradually reduced to 28.1 tons/h at 1500; sulphur content in the fuel, 3.7%. The plume was labelled with about 33 kg of uniformly released SF_6 in the period 1320-1420.

Airborne measurements: The measurements comprised NO_x, SO_2 and SF_6 concentrations. The SF_6-meter was used for the first time and the measurements mainly concerned controls and a comparison between the responses of different instruments. The plume was first localized in three traverses at about 4 km from the plant, whereafter SF_6 was released and a further 7 traverses were made at distances between 4 and 10 km. Measurements were then terminated because the wind dropped.

Results: Figure 21 shows plume profiles for NO_x, SO_2 and SF_6 concentrations. The position of the peaks was corrected for instrumental delay times (cf. sects. 3.3, 3.2, and 3.1). Considering that the three instruments have different response times (1.4, 4 and 4 s, respectively), the agreement is satisfactory.

6.5. Flight No. 7602; 5 March 1976

Weather: A weak cold front with low-lying clouds passed the area; the wind velocity was about 6 m/s with direction ENE. Radiosonde measurements at Jægersborg indicated neutral conditions.

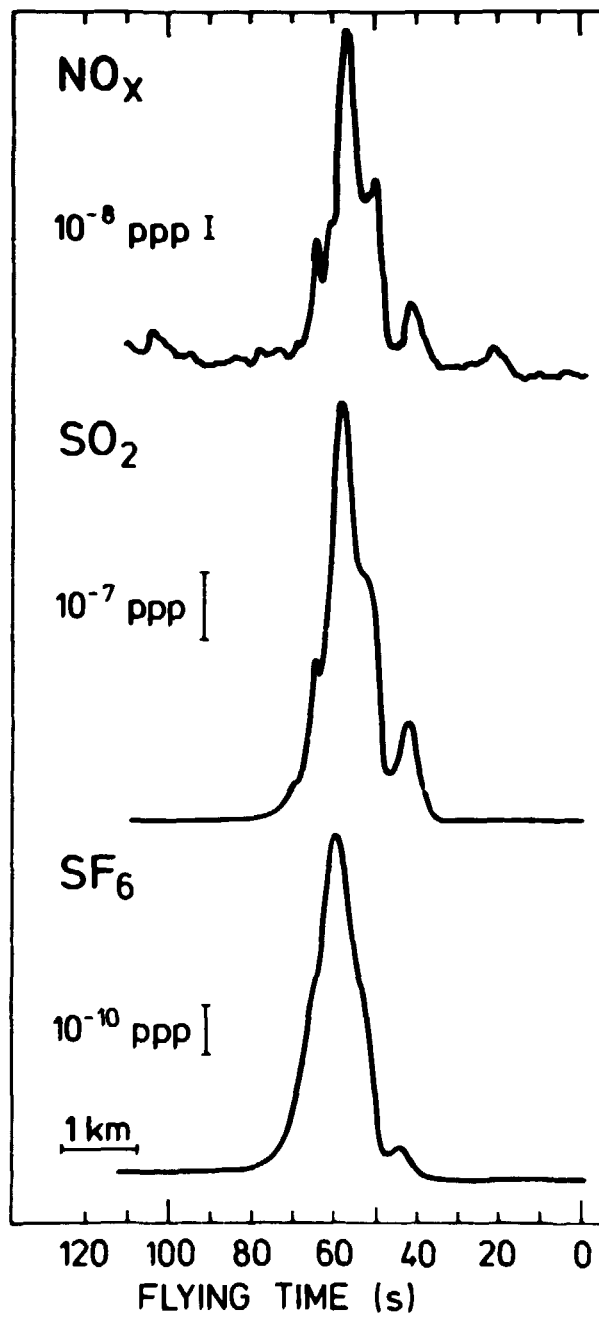

Fig. 21. Plume profiles recorded simultaneously with NO_x, SO_2 and SF_6 instruments on 4 March 1976. The plume was scanned from north (right) to south (left) with a velocity of 196 km/h, 9 km from the power plant at a height of 440 m. The positions of the profiles are corrected for instrumental time delays of 4, 6 and 13 s, respectively.

Power plant: Block 1 was shut down and block 2 was running with a fuel consumption of 58 tons/h; sulphur content in the fuel, 3.6%. The plume was labelled with SF_6 by release of about 33 kg in the period 1250-1350.

Airborne measurements: The instrumentation was the same as for flight No. 7601, but unfortunately the SO_2-detector broke down before any traverses were performed. The localization of the plume required 8 traverses. The plume profiles for NO_x and SF_6 concentrations were determined at 7 distances between 10 and 40 km. Measurements were then terminated because of clouds at the altitude used for the flight.

Results: Firstly, it was demonstrated that SF_6 could be traced at distances up to at least 40 km. Secondly, it appeared that the ratio of the NO_x and SF_6 concentrations was independent of the distance from the plant (Fig. 22); this suggests that NO_x can be used as a conservative tracer.

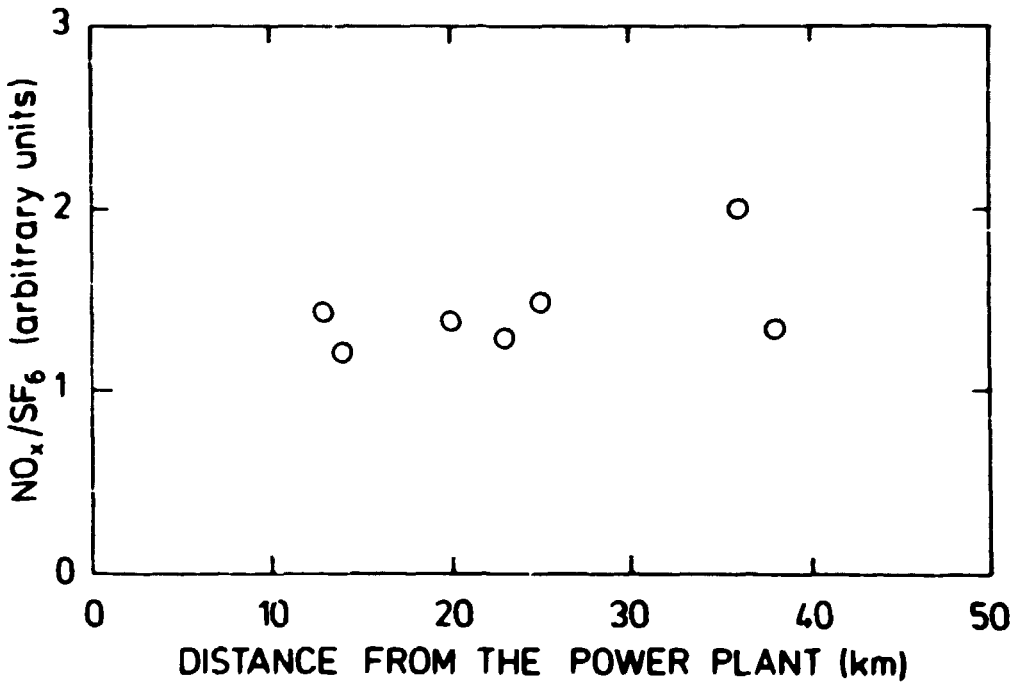

Fig. 22. The ratio between integrated SF_6 and NO_x concentrations as a function of the distance from the power plant. The measurements were performed on 5 March 1976. The wind speed was 6 m/s; thus 1 km corresponds to a travel time of about 2.8 min. Wind direction ENE.

7. CONCLUSION

The Danish contribution to the COST 61a project aimed at a detailed investigation of plume parameters. By the end of the project period proper, all experimental techniques had been developed and at least tested in the laboratory. However, the results obtained were only preliminary and should be treated accordingly; the main reason for this delay lies in the fact that the use of the radioactive ^{35}S-tracer had to be postponed due to public reaction. Attempts to use results of inactive analysis (tables 1 and 2) yielded no meaningful results; probably because the varying background could not be subtracted.

From the experiments on 5 March 1976 (Fig. 22), it appeared that NO_x can be used as an inner tracer; therefore the decrease of the SO_2/NO_x ratio depicted on Fig. 19 reflects a genuine loss of SO_2 from the plume with time. The loss of SO_2 between 4.3 and 21.5 km (a travel time of about 24 min is estimated) from the stack corresponded to about 50%. The deposition of SO_2 is much too slow to account for this effect, which we therefore tentatively ascribe to oxidation. The loss rate observed is about the largest ever seen; it may have been the result of a combination of bright sunshine and high concentrations of other components in the plume.

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